CHEMICAL VALORIFICATION OF AGRICULTURAL RESIDUES – CORN STALKS

VALORIFICAREA CHIMICĂ A REZIDUURILOR AGRICOLE - TULPINI DE PORUMB

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Abstract. *The chemical industry has shown a growing interest in the valorisation of agricultural residues, specifically cereal byproducts, for their potential in the pulping and papermaking industry. This interest is driven by the abundance and cost-effectiveness of these residues. This study explores the chemical composition of corn stalks, providing compelling evidence for their potential as a feedstock in the chemical industry for the production of papermaking fiber. Various alkaline pulping processes, employing different cooking agents, were examined for their effectiveness in converting corn stalks. The study's findings highlight the potential of using this cheap raw materials to produce high-value bio-based materials, offering substantial cost savings for the pulp and paper industry.*
Key words: *corn stalks, pulp and paper, cellulose, lignin.*

Rezumat. *Industria chimică manifestă un interes din ce în ce mai mare pentru valorificarea reziduurilor agricole, pentru potențialul acestora în industria de prelucrare a celulozei și a hârtiei. Acest interes este determinat de abundența și rentabilitatea acestor reziduuri. Acest studiu explorează compoziția chimică a tulpinilor de porumb, oferind dovezi convingătoare pentru potențialul lor ca materie primă în industria chimică pentru producția de fibre pentru fabricarea hârtiei. S-au examinat diferite procese alcaline care utilizează diferiți agenți de delignificare, pentru eficacitatea lor în transformarea tulpinilor de porumb. Concluziile studiului evidențiază potențialul utilizării acestor materii prime ieftine pentru a produce bio materiale de mare valoare, oferind economii substanțiale de costuri pentru industria celulozei și hârtiei.*
Cuvinte cheie: *tulpini de porumb, pastă și hârtie, celuloză, lignină.*

INTRODUCTION

Corn, also known as maize (*Zea mays* ssp. *mays* L.), is a globally cultivated crop, primarily used for food, animal feed, and bioenergy production. Despite its widespread use, a significant portion of the plant remains underutilized or completely unused. (Ungureanu *et al*, 2020). The above-ground residue left behind after the corn kernels have been harvested, comprising of stalks and leaves,

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accounts for approximately half of the total biomass yield of a corn crop. Typically, it is left in the fields and needs to be plowed under soil to prepare the field for the subsequent crop. However, farmers have the option to gather it for various uses such as winter fodder for ruminants, livestock bedding, a bioenergy source, or as a raw material for bioproducts, cellulosic ethanol fermentation, fiber production, and more. (Chesca *et al.,* 2018a; 2018b).

The conversion of stalks into fibrous materials, apt for unbleached paper grades, paperboard, board, and molded pulp, is a topic that is rarely touched upon in literature studies (Puițel *et al.,* 2020). Despite this, the potential is immense. With substantial quantities of this raw material available each year, it presents itself as a viable alternative to virgin fibers, recycled papers, and plastics. (Măluțan *et al.,* 2017).

The study aims to convert renewable biomass residues, which are by-products of agricultural processes, into value-added products. The report presents the successful conversion of corn stalks into papermaking pulps using various techniques, and advocates for their use in bio-based packaging products. The experimental work primarily used alkaline methods due to their effectiveness in lignin removal and their ability to produce high-strength fibers.

MATERIAL AND METHOD

The following materials have been used:

- corn stalks were manually harvested from local farms in Vaslui County.

Then the stalks were processed: they were chopped, air-dried until they reached atmospheric equilibrium, and further cut into smaller pieces, approximately 3 - 5 cm in length, to aid in impregnation.

The findings of the study were based on the oven-dry weight of the material. All the reagents employed in the study were of analytical grade. It's important to note that no process or functional additives or other chemicals were used to enhance the manufacturing process or the properties of the paper products.

Work procedure*:*

- The material was grounded and prepared for a series of chemical analyses conducted using established standardised TAPPI methods: holocellulose (as per T 9 wd-75, 1975); cellulose (following T 17 wd-70, 1970); pentosans (in accordance with T 223 cm - 01, 2001); lignin (using T 222 om - 02, 2002); acetone extractives (as per T 264 cm - 07, 2007); hot water solubility (following T 207 cm - 99); 1% NaOH solubility (as per T 212 om - 02) and ash content (using T 211 om - 02, 2002). (Tofănică *et al*, 2011).

Pulping experiments were conducted in a laboratory-grade rotating batch reactor made of stainless steel, outfitted with electric heating and an automatic temperature control system. The trials utilized 400 g of raw materials (on an oven-dry mass basis), and a corresponded pulping liquor at a solid-to-liquid ratio of 5:1. A total of six pulping experiments were executed, each employing different cooking agents as detailed in table 1. Across all six experiments, a consistent set of conditions was maintained: a heating duration of 30 minutes and a cooking period of 60 minutes at a temperature of 170 °C.

RESULTS AND DISCUSSIONS

The chemical composition of corn stalks, as shown in table 1, displays promising results when compared to other commonly used non-wood, softwood, and hardwood materials. The primary constituents of the stalks are carbohydrates, with cellulose making up approximately 40 %, and pentoses and hexoses each contributing around 20 %. This composition makes corn stalks a valuable resource for technological advancements in the production of bio-based materials and chemicals.

The chemical analysis also uncovered a Klason lignin content of about 20 %, a figure that aligns with those found in other annual plants. The composition of corn stalks makes them an ideal candidate for the production of papermaking pulps, without necessitating extra cooking time or chemical input compared to other non-wood materials. Furthermore, the levels of extractives and ash in corn stalks are comparable with those found in other annual plants, agricultural and industrial crops, and agricultural residues (tab. 1).

Table 1

Chemical composition of corn stalks compared with other agricultural residues
(Tofanică *et al.,* 2011; Puițel *et al*., 2017)

Properties	Agricultural residues		
	Corn stalks (current research)	Rapeseed stalks, %	Wheat straw, %
Cellulose	39	40	43
Pentosans	20	23	29
Hollocellulose	64	72	
Lignin	20	21	18
Extractives	3	7	6
Ash	5	6	6

The results obtained after the analysis of the pulps in terms of fiber yield, total yield are presented in table 2. Screened yield refers to the amount of usable pulp obtained after the pulping and screening processes. A high screened yield indicates that a large proportion of the corn stalks was successfully converted into usable pulp, further highlighting the effectiveness of corn stalks as a raw material for pulping.

Table 2

Pulping yield of corn stalk compared with other agricultural residues

Sample	Alkali charge, %	Temperature, °C	Screened yield, %	Rejected, %	Total yield, %
Corn stalks	18	170	36	0	36
Rapeseed stalks	18	170	38	1	39
Rapeseed stalks	20	170	39	0	39
Wheat straw	20	170	39	1	4

The proposed pulping trials conducted on corn stalks have yielded valuable results. The trials have produced high-quality pulp fibers, which are essential for creating durable and sustainable paper products. These fibers have

the potential to replace traditional wood-based fibers, offering a more sustainable and environmentally friendly alternative.

The yield from corn stalks in the pulping process is comparable to that of other agricultural residues such as wheat straw and rapeseed stalks, demonstrating its potential as a viable alternative raw material in the pulp and paper industry. This similarity in yield underscores the versatility of agricultural residues as a resource, opening up new possibilities for sustainable practices in the industry.

CONCLUSIONS

1. The comprehensive chemical analysis conducted on corn stalks has shed light on the potential of this agricultural byproduct. Their unique composition, rich in carbohydrates, makes them an excellent candidate for sustainable and efficient use in chemical industry, thereby paving the way for innovative uses of this abundant resource.

2. The delignification process of corn stalks revealed that this type of raw material is adequate for pulping. The proposed pulping trials returned valuable pulps fiber and screened yields.

3. The results indicate that corn stalks are not only suitable but also a promising raw material for the chemical industry, specifically in the pulping process.

REFERENCES

1. **Chesca A.M., Nicu Raluca., Tofănică B.M., Puițel A.C., Vlase R., Gavrilescu D., 2018a** - *Optimization of Soda Pulping Process of Corn Stalks by Response Surface Modelling*, Cellul. Chem. Technol., 52 (9-10), pp. 823-831.
2. **Chesca A.M., Nicu Raluca, Tofănică B.M., Puițel A.C., Vlase R., Gavrilescu D**., **2018b** - *Pulping of Corn Stalks - Assessment in Bio-Based Packaging Materials*, Cellul. Chem. Technol., 52 (7-8), pp. 645-653.
3. **Măluțan T., Puițel A.C., Tofănică B.M., Custură A.E., 2017** - *Biorefining of Lignocellulosic Materials, in Corrugated Cardboard Packaging for Food - Handbook of Good Practice,* Ed. Politehnium, Iași, pp.112.
4. **Puițel A.C., Moisei N., Tofănică B.M., Gavrilescu D., 2017** - *Turning Wheat Straw in a Sustainable Raw Material for Paper Industry*, Environ. Eng. Manag. J., 16 (4), pp.1027-1032.
5. **Puițel A.C., Tofănică B.M., Gavrilescu D., 2020** - *Fibrous raw materials from agricultural residues, in Pulp Production and Processing - High-Tech Applications,* Ed. Walter de Gruyter, Berlin, pp. 92.
6. **Tofănică B.M., Puitel A.C., Gavrilescu D., 2011** - *Nonwoods: fiber sources for papermaking pulp production. Laboratory trials*, Bul. Inst. Polit. Iasi, 57 (3), pp. 127-140.
7. **Ungureanu O.C., Stana I.O., Ungureanu Elena., Bota Viviane Beatrice, Turcuș Violeta, 2020 -** *Research on morphological, biochemical and productivity aspects of some corn genotypes (Zea mays L.) in pedoclimatic conditions in the Arad area,* Studia Univ. VG, SSV. Arad, 30 (4), pp. 163-168.